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HYBRID ORGANIC-INORGANIC PHOTOREFRACTIVES (Preprint)

D.R. Evans, G. Cook, J.L. Carns, and M.A. Saleh

AUGUST 2006

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14. ABSTRACT
Surface space charge field modulates the local liquid crystal alignment.
Liquid crystals amplify the refractive index modulation.
Highlights the opportunity of exploiting the electric field sensitivity and large birefringence of liquid crystals.

15. SUBJECT TERMS
Organic, Inorganic, Photorefractive

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Hybrid Organic-Inorganic Photorefractives

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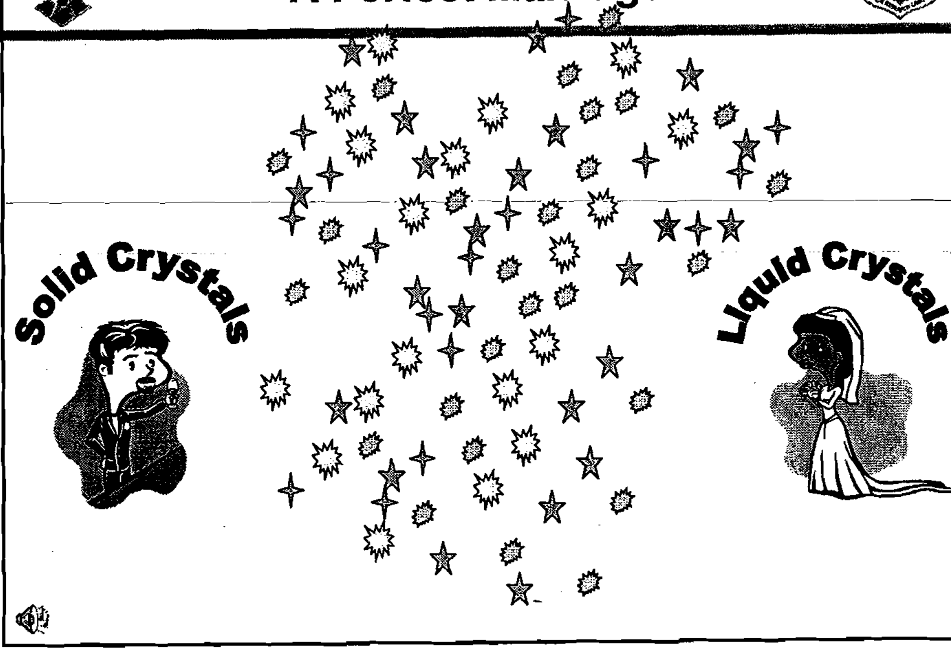
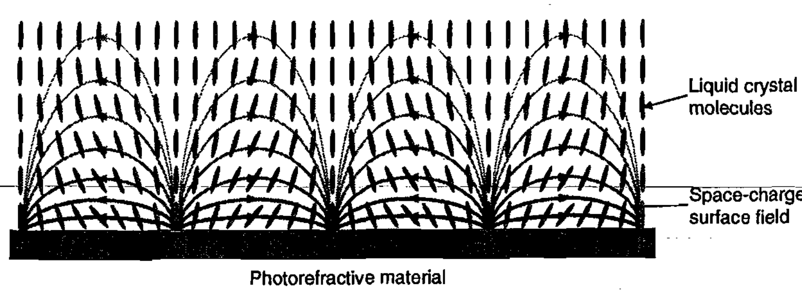
A Perfect Marriage



Outline

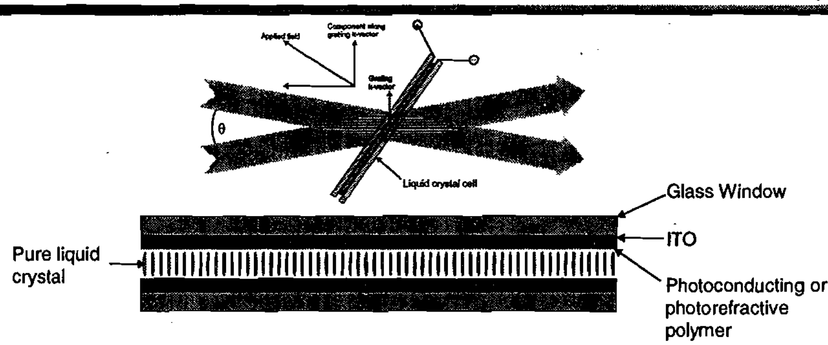
- Concept
- Materials selection
- Outline theory
- Cell construction
- Early results
- New results
- Poling issues
- Rotated cells
- Summary

Concept



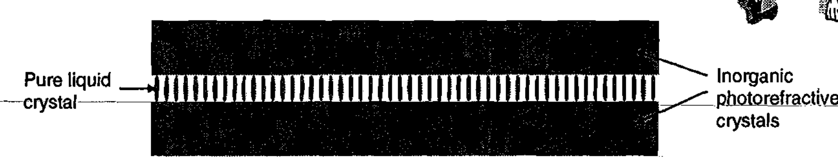
- Concept and theory
  - L.C. Reorientation from a single window - N. V. Tabiryan, C. Umeton, JOSA B, 15, 7, 1912-1917, 1998
  - Beam coupling from a dual window device - D. C. Jones, G. Cook, Opt. Commun., 232, 399-409, 2004
- Surface space charge field modulates the local liquid crystal alignment
- Liquid crystals amplify the refractive index modulation
- Highlights the opportunity of exploiting the electric field sensitivity and large birefringence of liquid crystals

Polymer Version



- S. Bartkiewicz, K. Matczyszyn, A. Miniewicz, F. Kajzar, Opt. Comm., 187, 257-261, 2001
- Very high gain coefficient, but......
    - Small grating phase shift (drift dominated charge migration)
    - Applied fields
    - Tilted optical geometry
    - Small beam intersection angles (low trap density) - Raman-Nath regime only

Inorganic-Organic Hybrids



- G. Cook, C. A. Wyres, M. J. Deer, D. C. Jones, SPIE vol. 5213, pp 63-77, 2003.
- Space charge field is governed by the inorganic crystal properties
- 90 degree grating phase shift possible
- Normal incidence operation
- No applied fields - entirely passive device
- Large beam intersection angles (trap density) - Bragg regime possible

Inorganic Choices

- $Fe:LiNbO_3$
  - Insensitive
  - Problems with photovoltaic beam fanning
  - Charge migration is dominated by the photovoltaic effect (drift)
  - Phase shift is poor unless space charge field saturates (difficult at coarse grating spacing)
- BSO/BGO
  - Very sensitive and high speed
  - Excellent charge diffuser and photoconductor
  - Optically active
- $Fe:KNbO_3$ and SPS
  - Very sensitive and high speed (Fe/Ni/Ag etc. $KNbO_3$ and Te:SPS)
  - Good charge diffusers and photoconductors
  - Maybe difficult to obtain in large sizes (but we're working on that!)
  - Relatively small ($KNbO_3$) or near zero (SPS) photovoltaic effect
- Ce:SBN
  - Quite sensitive
  - Charge migration is dominated by diffusion - phase shift approaches 90 degrees
  - No complications from photovoltaic effects

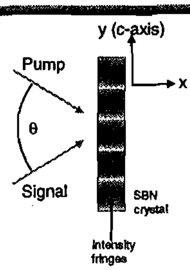
Organic Choices

- Lots!
  - Homeotropic
  - Planar
  - Twisted
  - Bend
  - Splay
  - Planar/homeotropic
- 100's of possible liquid crystals, many possible phases
  - Nematic
  - Smectic
  - Ferroelectric
- Probably best to avoid ionic liquid crystals
  - Possible screening charge problems
  - Fluorinated liquid crystals look good

Outline Theory (SBN)

- Intensity fringes

$$I(y)=\left(I_{signal}+I_{pump}\right)\left(1+\frac{A_{signal}A_{pump}^{*}}{I_{signal}+I_{pump}}\cos(2\theta)\exp\left(i2k\sin(\theta)\,y\right)+c.c\right)$$



- Space charge field

$$E_S=\frac{iE_D}{1+E_D/E_Q}m$$

$$E_D=2\pi k_bT/e\Lambda$$

$$E_Q=eN_A\Lambda/2\pi\varepsilon_s$$

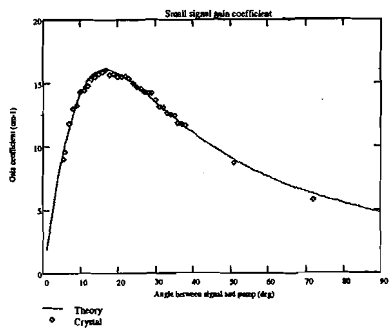
$$N_A=\frac{\varepsilon_s k_b T}{\left(L_D e/2\pi\right)^2}$$

$$m=\frac{2\sqrt{I_{pump}I_{signal}}}{I_{pump}+I_{signal}}\cos(2\theta)$$

- Exponential gain coefficient

$$\Gamma=\frac{2\pi}{\lambda}n^3 r_{eff}\,\mathrm{Im}(E_S)$$

$$r_{eff}=r_{33}\cos^2(\theta)-r_{13}\sin^2(\theta)+\left(\frac{n_e-n_o}{n_e}\right)(r_{33}+r_{13})\sin^2(2\theta)$$



Outline Theory (Liquid Crystal)

- Electrostatic potential

$$V(x,y)=\frac{1}{2}\frac{iE_s}{K}e^{(iKy-Kx)}+c.c.$$

- Electric torque

$$\mathbf{F}_E=\Delta\varepsilon(\hat{n}\cdot\mathbf{E})(\hat{n}\times\mathbf{E})$$

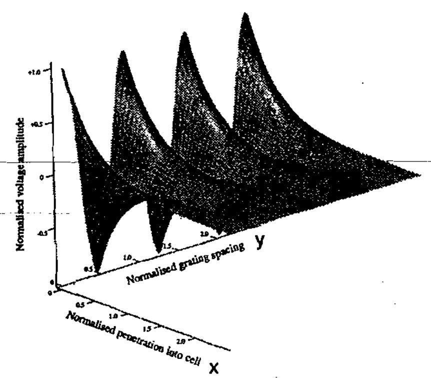
- Elastic torque

$$\mathbf{F}_L=\hat{n}\times(\mathbf{E}_1+\mathbf{E}_2+\mathbf{E}_3)$$

- Refractive index modulation

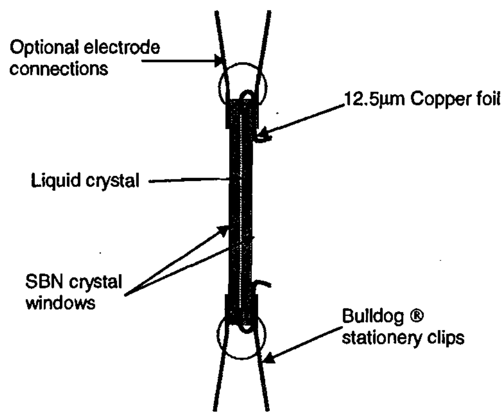
$$n=\frac{n_o n_e}{\sqrt{n_o^2\sin^2(\beta\pm\theta)+n_e^2\cos^2(\beta\pm\theta)}}$$

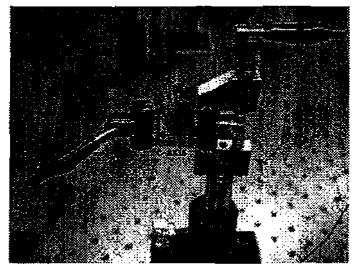
$\mathbf{E}_1$, $\mathbf{E}_2$ and $\mathbf{E}_3$ are the molecular fields associated with bend, splay and twist deformations respectively



- Steady state molecular reorientation is achieved when $\mathbf{F}_E=\mathbf{F}_L$
- Space-charge field penetrates ~1.5 - 2.0x grating spacing
- Intermolecular elastic forces permit longer range influence

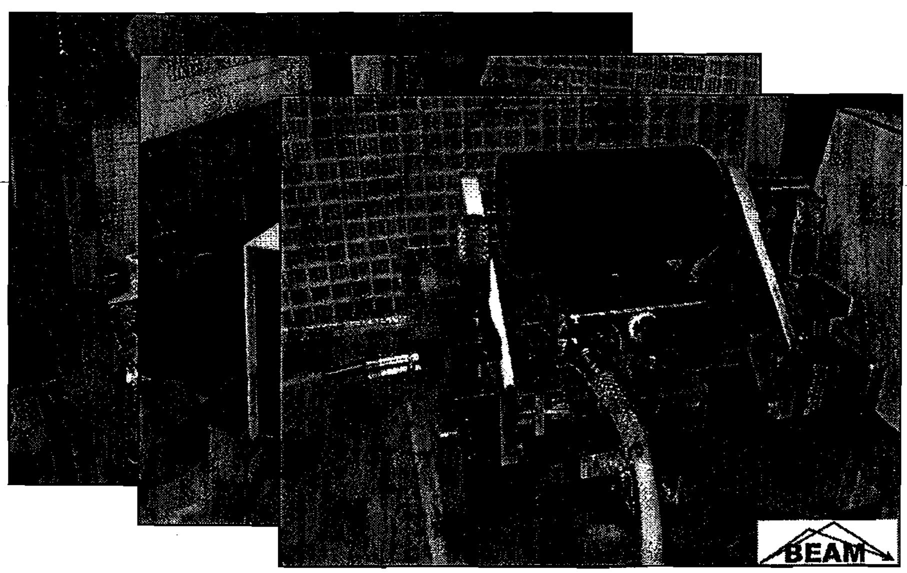
Preliminary Cell Construction



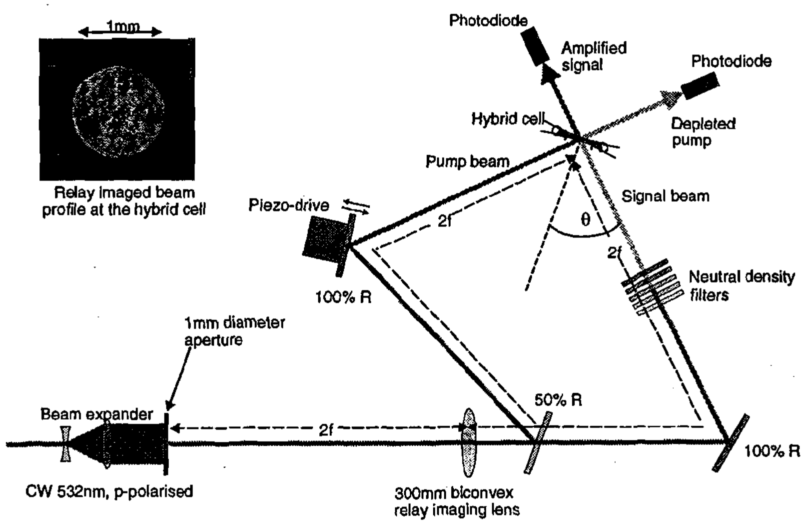


G. Cook, C. A. Wyres, M. J. Deer, D. C. Jones, "Hybrid organic-inorganic photorefractives", SPIE vol. 5213, pp 63-77, 2003.

Cell Preparation

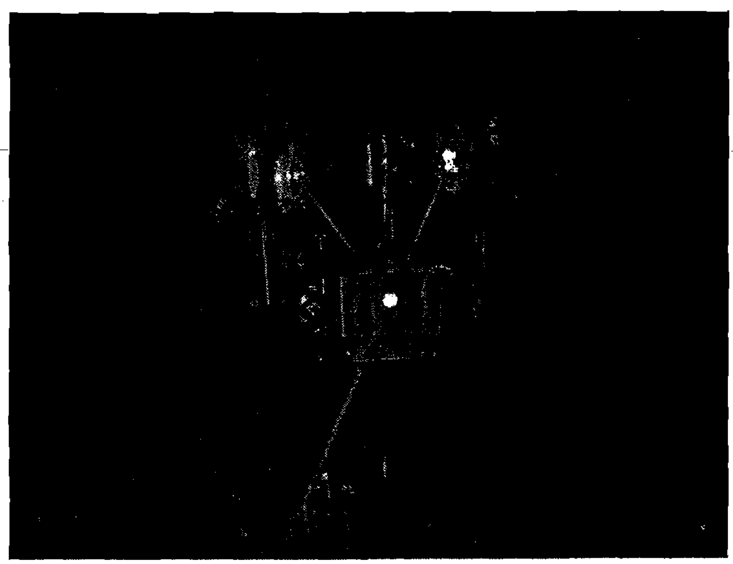


Preliminary Experiments

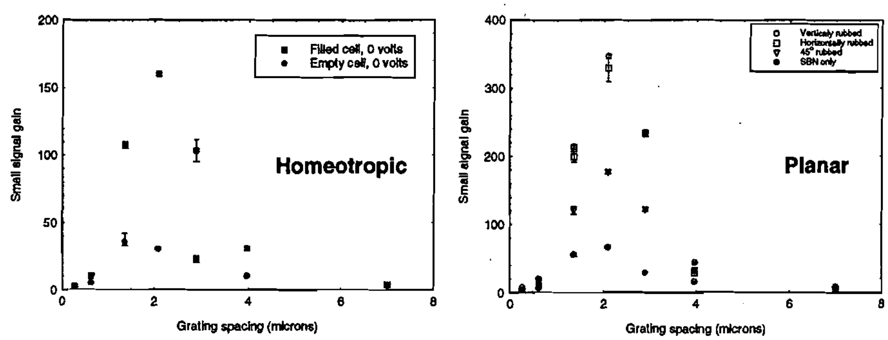


G. Cook, C. A. Wyres, M. J. Deer, D. C. Jones, "Hybrid organic-inorganic photorefractives", SPIE vol. 5213, pp 63-77, 2003.

Works!



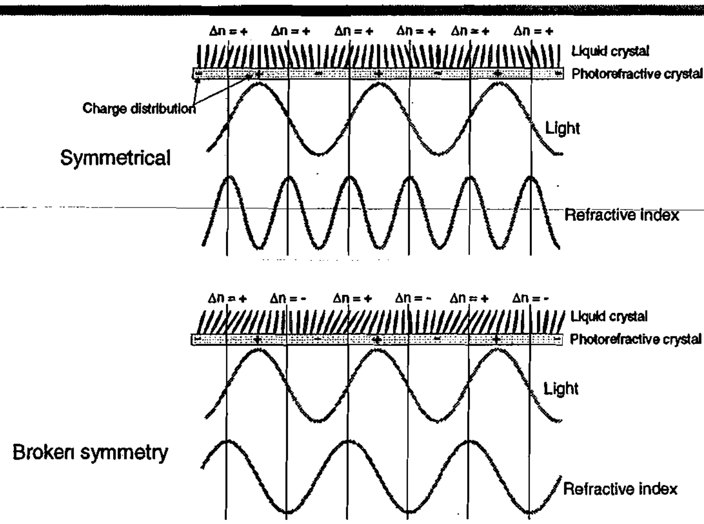
Preliminary Results with Nematics



- Works! ← but it should not have worked!
- Full Bragg matching
- 90 degree grating phase shift
- Sensitive to alignment (Etalon effects)

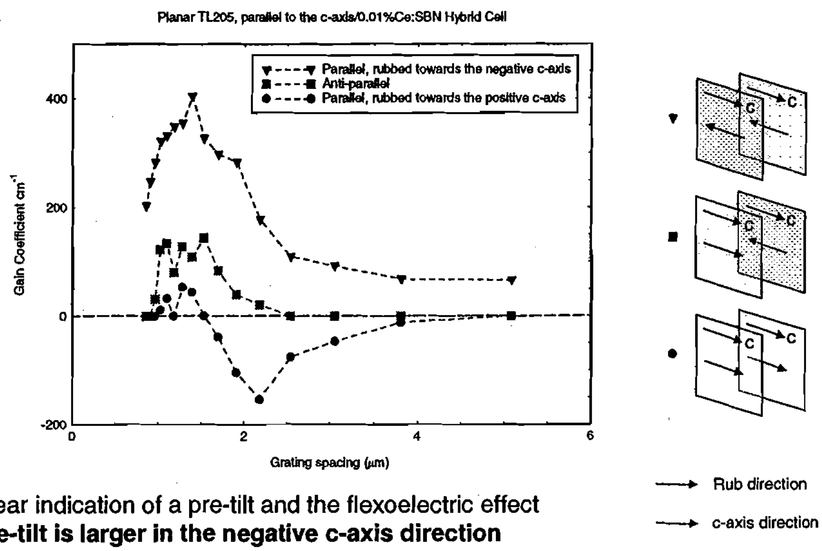
G. Cook, C. A. Wyres, M. J. Deer, D. C. Jones, "Hybrid organic-inorganic photorefractives", SPIE vol. 5213, pp 63-77, 2003.

Molecular Alignment Issues



- Glass test cells show no pre-tilt, so the symmetry should not be broken
- Needs a broken symmetry and a molecular polarity to work
- Nematics do not have a polarity

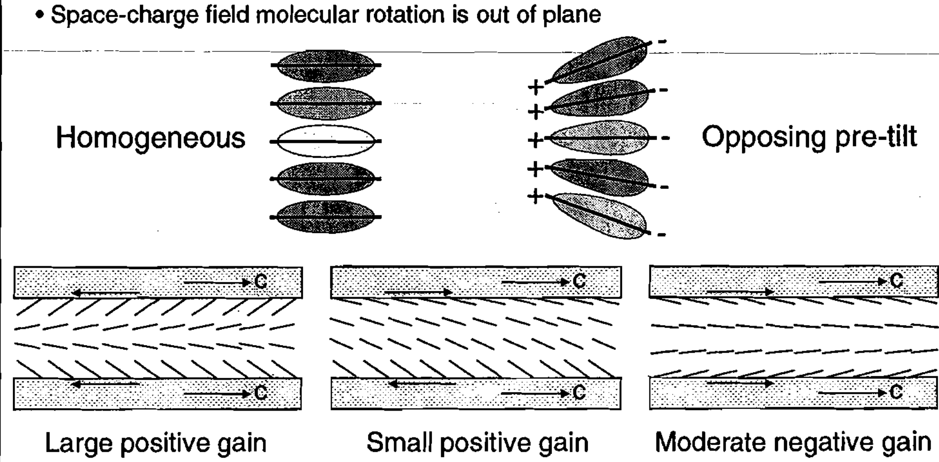
New Results
C-parallel Nematic Cell



- Clear indication of a pre-tilt and the flexoelectric effect
- **Pre-tilt is larger in the negative c-axis direction**
- **Pre-tilt direction follows rubbing direction**

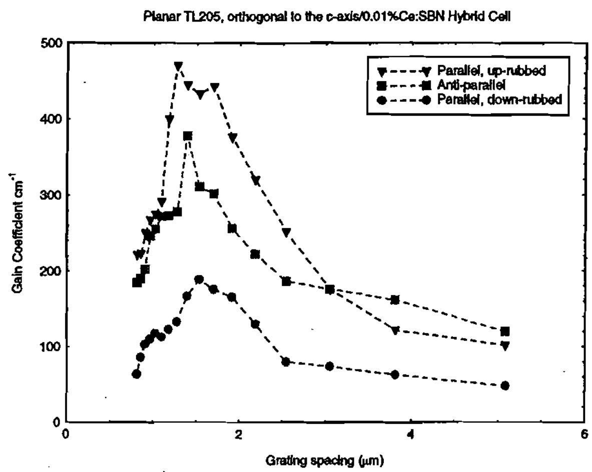
C-parallel Nematic Cell Dynamics

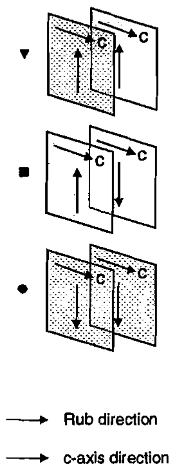
- Van der Waal's forces from crystal induce a pre-tilt*
- Pre-tilt provides the required molecular asymmetry
- Flexoelectric effect provides molecular polarity
- Space-charge field molecular rotation is out of plane



* A. L. Alexe-Ionescu, R. Barberi, J. J. Bonvent, M. Giocondo, "*Nematic surface transitions induced by anchoring competition*", Phys Rev. E, vol. 54, no. 1, pp 529-535,1996

New Results
C-orthogonal Nematic Cell



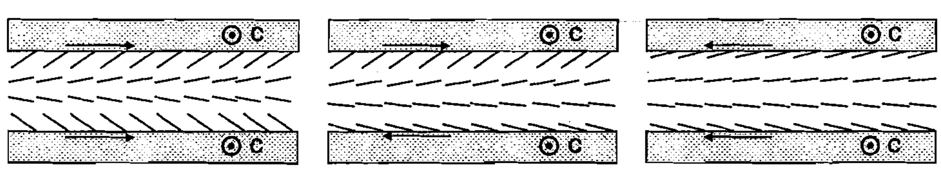


- Clear indication of a pre-tilt and the flexoelectric effect
- **Pre-tilt is larger in the "up" direction**
- **Pre-tilt direction is independent of the rubbing direction**

C-orthogonal Nematic Cell Dynamics

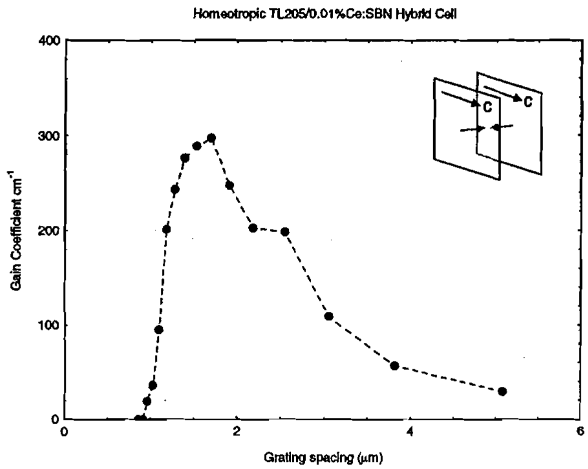
- Space-charge field molecular rotation is an in-plane twist

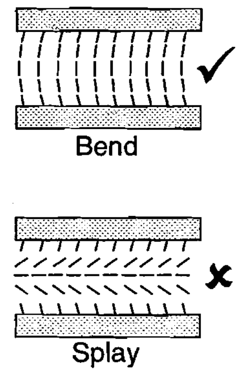
Rub Up - up	Rub Up - down	Rub Down - down



Large positive gain	Moderate positive gain	Small positive gain

New Results
Homeotropic Nematic Cell





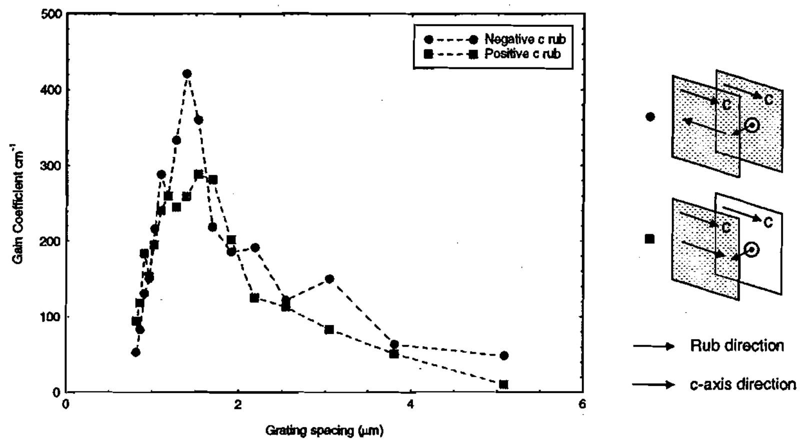
- Clear indication of a pre-tilt and the flexoelectric effect
- Low gain implies a small pre-tilt with bend rather than splay alignment

New Results

- Having identified a crystal substrate induced pre-tilt, choose alignment schemes to maximize this effect.........

New Results
Hybrid Nematic Cell 1

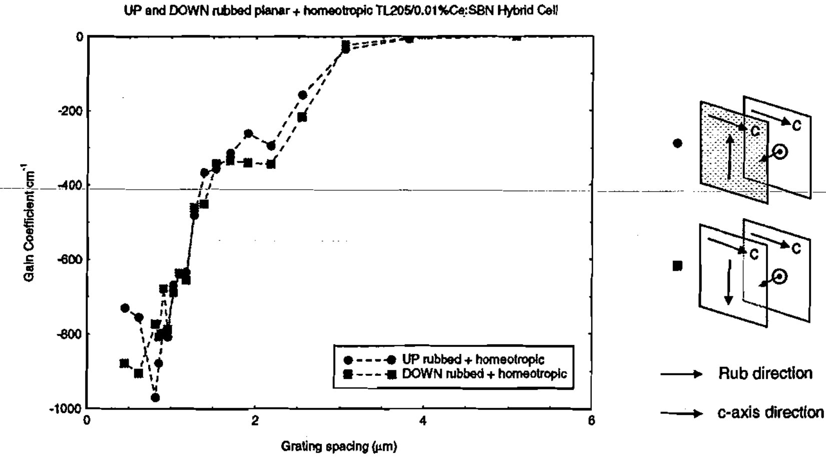
Parallel c planar + homeotropic TL205/0.01%Ce:SBN Hybrid Cell



- Pre-tilt direction and magnitude depends on the c-axis rubbing direction
- But gain always remains positive so homeotropic layer dominates cell alignment
- Slightly better with a negative rub
- **Homeotropic layer is therefore pre-tilted towards the negative c-axis**

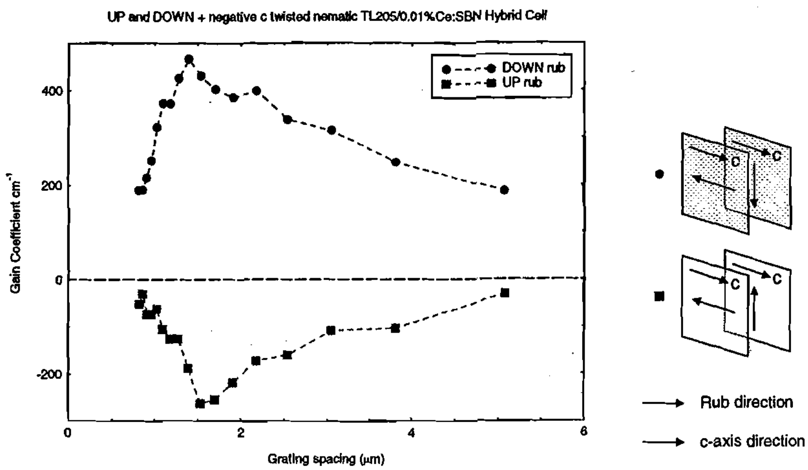
New Results
Hybrid Nematic Cell 2

UP and DOWN rubbed planar + homeotropic TL205/0.01%Ce:SBN Hybrid Cell



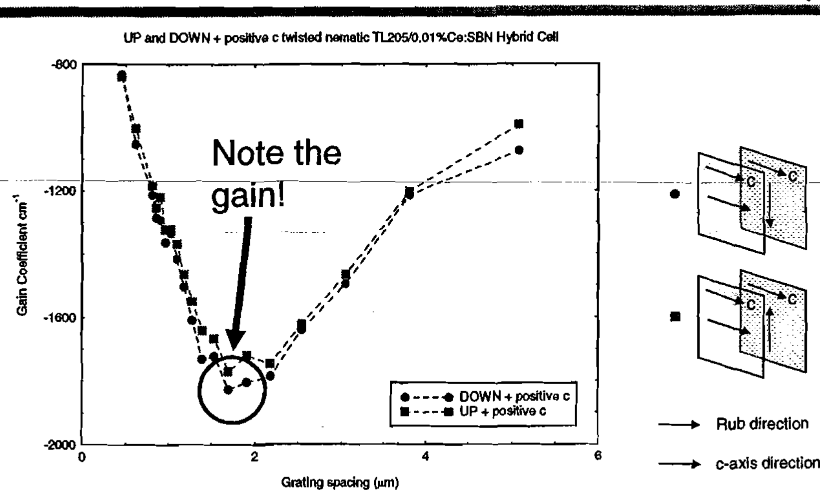
- Pre-tilt magnitude (not direction) depends on the up/down rubbing direction
- Homeotropic layer is pre-tilted towards the negative c-axis (previous slide)
- Gain always remains negative, no difference between up or down rub (homeotropic dominates)
- **Combination of orthogonal pre-tilts gives a twisted hybrid alignment**

New Results
Twisted Nematic Cell



- Twist direction reverses (odd – only the a axis pre-tilt magnitude changes with rubbing direction)
- Twist direction determines the gain direction from the flexoelectric effect
- Larger pre-tilts reduce the twist "tension" and the flexoelectric effect
- Pre-tilt is larger in the "up" direction, so gain is less for "up" rubbed cells

New Results
Twisted Nematic Cell



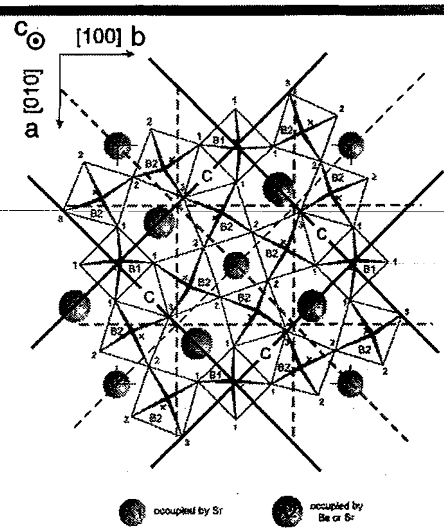
- Twist direction is constant (a-axis rub direction changes just the pre-tilt magnitude)
- Smaller pre-tilts increase the twist "tension" and the flexoelectric effect
- Positive c rub has smaller pre-tilt than negative c rub, so gain is increased
- Pre-tilt is larger in the "up" direction, so gain is less for "up" rubbed cells

Pre-tilt Summary

- C-parallel planar: bidirectional c-axis pre-tilts, largest for negative c rub
- C-orthogonal planar: unidirectional a-axis pre-tilt, largest for “up” rub
- Homeotropic: c-axis pre-tilt
- Hybrid c-parallel planar/homeotropic: c-axis pre-tilts
- Hybrid c-orthogonal planar/homeotropic: a and c-axis pre-tilts
- Twisted nematic: a and c-axis pre-tilts

Cause?

SBN Crystal structure



Oxygen atoms at the vertices of the polyhedra

J Wingbermuhle, M Meyer, O F Schirmer, R Pankrath, R K Kremer, “*Electron paramagnetic resonance of Ce3+ in strontium–barium niobate*”, J. Phys.: Condens. Matter, vol 12, pp 4277–4284., 2000.

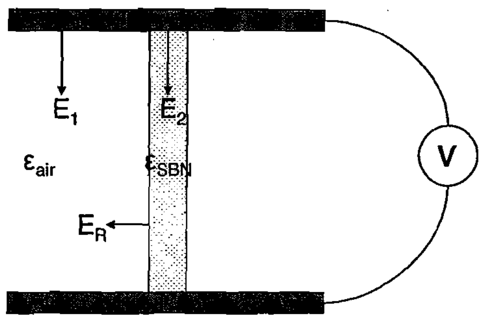
The structure of SBN as seen along the *c*-axis, [001]. The right angles at the four outer A1 sites delineate boundaries of the unit cell. The ionic positions and the symmetry elements are indicated: full lines mark the traces of mirror planes, dashed ones those of glide mirror planes. The designation A1 labels sites preferred by Sr, A2 those occupied by Ba or Sr. The sites C are empty in the ideal structure. B1 and B2 are the two types of Nb position. The numbers at the corners of the O2− octahedra mark O2− ions and their equivalences. The *z*-coordinates of the O2− ions labelled 1, 2 and 3 as well as of the Nb ions B1 and B2 are close to zero. The other ions, Sr and Ba, at A1 or A2, as well as the O2− ions at perspectively thickened apexes of the B1 and B2 octahedra, lie at approximately 12 of the lattice constant *c*, 3.91 Å. The crosses mark oxygen positions at −12 *c* below the plane.

SBN Poling

- Crystal structure influences the liquid crystal pre-tilt
- Surface poling condition is therefore critical
- Typical poling method:

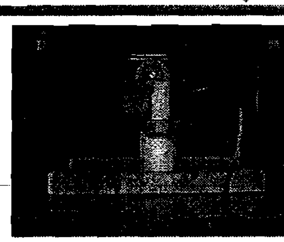
$E_1 \neq E_2$ if $\varepsilon_{air} \neq \varepsilon_{SBN}$

$E_R \neq 0$ if $E_1 \neq E_2$



SBN Poling

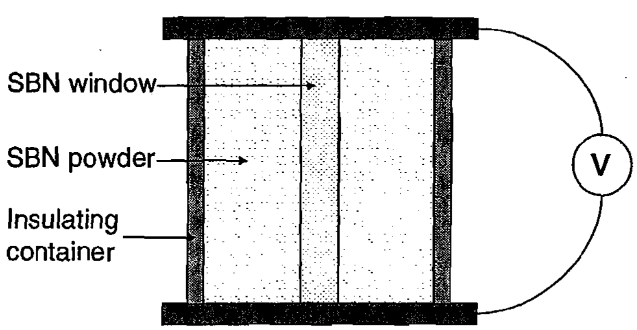
- Modified poling method:



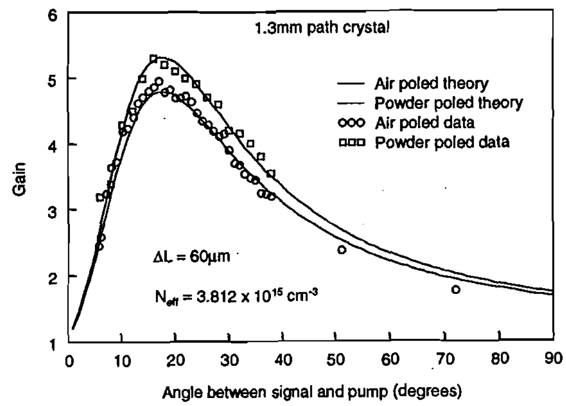
$\varepsilon_{\text{"air"}} \approx \varepsilon_{SBN}$

$E_1 = E_2$

$E_R = 0$

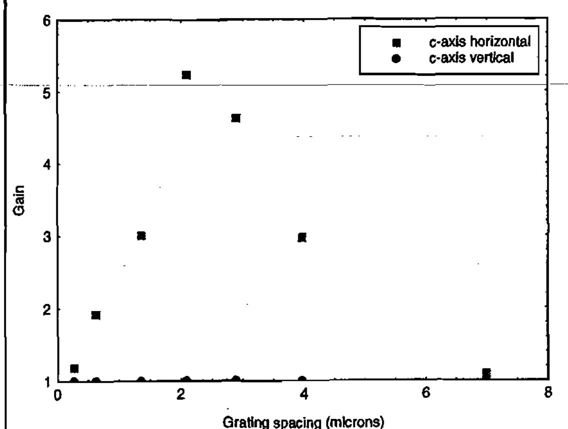


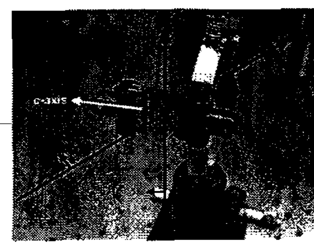
SBN Poling

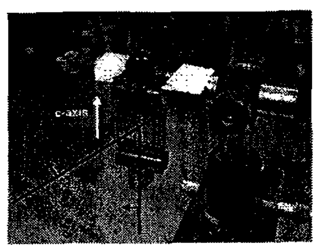


Rotated Cell Results

- Liquid crystal gain present only when the grating k-vector has a component along the SBN crystal c-axis



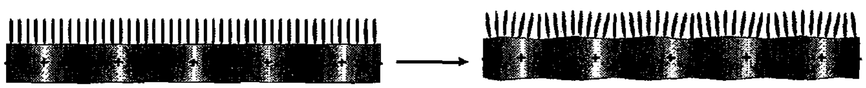




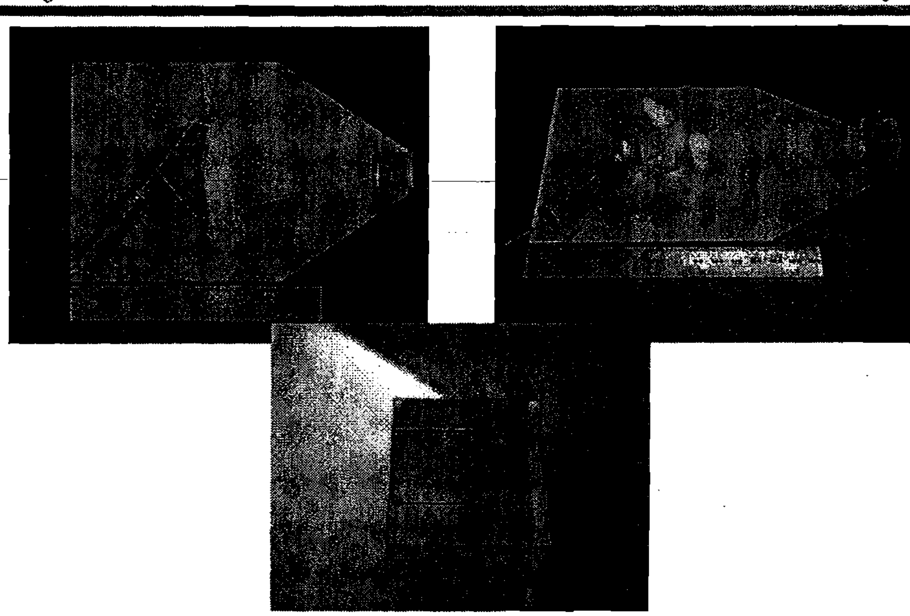
G. Cook, C. A. Wyres, M. J. Deer, D. C. Jones, "Hybrid organic-inorganic photorefractives", SPIE vol. 5213, pp 63-77, 2003.

Rotated Cell Results

- **Unexpected result**
  - Liquid crystal gain vanishes when SBN c-axis is othogonal to grating k-vector
    - SBN EO coefficients are zero
    - But the SBN diffusion field is still present!
    - Liquid crystal reorientation not driven directly by the diffusion field?
    - 90° phase shift strongly suggests the modulation mechanism is linked to charge diffusion
    - Piezoelectric?



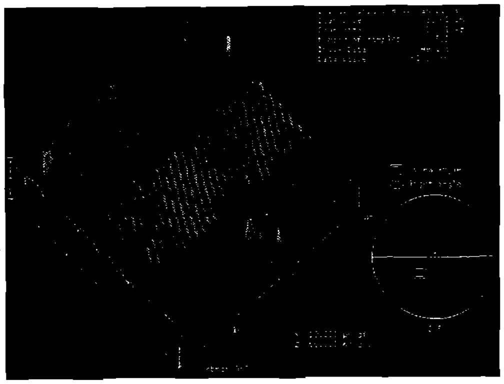
Piezoelectric Search



Piezoelectric Search

• AFM results......

Published surface field*



* E. Soergel, R. Pankrath, and K. Buse, "*Investigation of Photorefractive SBN Crystals with Atomic Force Microscopy*", *Ferroelectrics*, vol. 296, pp19–27, 2003

Space-Charge Field/Trap Density

• Found no evidence (yet) of piezoelectric surface deformations

↓

• If piezo effects are absent, LC must be driven by surface fields

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• Absence of LC beam coupling for k-vector at 90° to c-axis means an absence of a space-charge field

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• No space-charge field means either:
  • Zero charge diffusion across the c-axis (unlikely)
  • Negligible effective trap density across the c-axis (surprising)

Summary

- Highest Bragg matched gain coefficient for any photorefractive material (~1850 cm^{-1})
  - Full Bragg matching for grating spacings of ~400nm – 5μm.
  - 90° grating phase shift
- Surface pre-tilt and the flexoelectric mechanisms identified for unidirectional beam coupling
  - c-axis pre-tilt *direction and magnitude* depends on rubbing direction
    - Pre-tilt is greatest in the negative c direction
  - a-axis pre-tilt *magnitude* depends on the rubbing direction
  - Homeotropic alignment yields a pre-tilt towards the negative c-axis
  - SBN crystal structure is proposed as causing the pre-tilt through Van der Waal's forces
  - Poling quality is important for unidirectional gain (pre-tilt direction may otherwise vary)
- LC gain present only when a component of the grating k-vector lies along the c-axis
  - No evidence (yet) of piezoelectric induced LC alignment
  - Surface field induced LC alignment
  - No space-charge field for k-vector orthogonal to SBN c-axis – reason is unclear